

JC13 Rec'd PCT/PTO 25 APR 2005

We claim:

1. A process for preparing racemic metallocene complexes of the formula (I)

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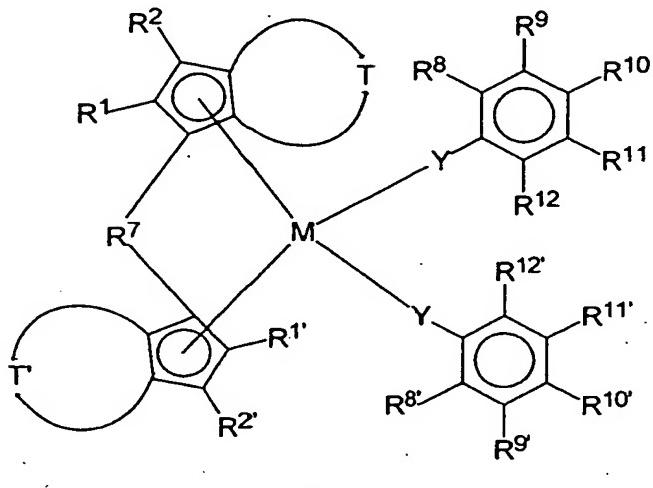
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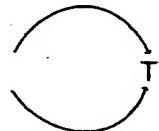
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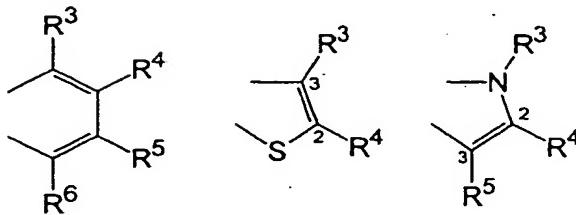
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where

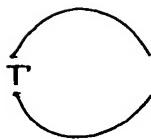


is a divalent group such as



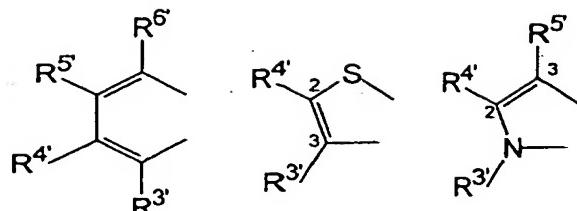
and

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is a divalent group such as

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and the substituents and indices have the following meanings:

20 M is titanium, zirconium or hafnium,

25 R¹, R², R³, R⁴, R⁵, R⁶, R⁹, R¹⁰, R¹¹, R¹, R², R³, R⁴, R⁵, R⁶, R⁹, R¹⁰, R¹¹ are identical or different and are each hydrogen, halogen, C₁-C₂₀-alkyl, 3- to 8-membered cycloalkyl which may in turn bear a C₁-C₁₀-alkyl group as substituent, C₆-C₁₅-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, arylalkyl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, -OR¹³, -SR¹³, -N(R¹³)₂, -P(R¹³)₂, or Si(R¹³)₃, where

30 R¹³ are identical or different and are each C₁-C₁₀-alkyl, C₆-C₁₅-aryl, C₃-C₁₀-cycloalkyl, alkylaryl, where the radicals mentioned may be partially or fully substituted by heteroatoms,

35 R⁸, R¹², R^{8'}, R^{12'} are identical or different and are each C₁-C₁₀-alkyl,

40 Y are oxygen -O-

R⁷ is a $[Z(R^{15})(R^{16})]_m$ -group, where

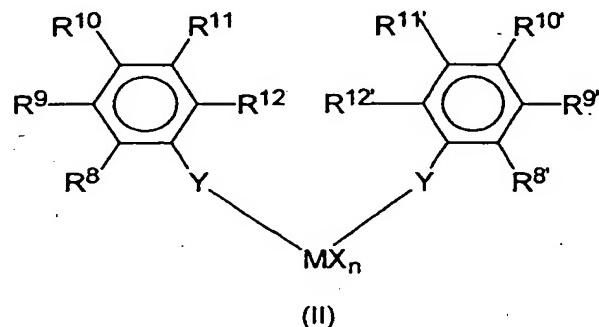
Z can be identical or different and are each silicon, germanium, tin or carbon,

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R¹⁵, R¹⁶ are each hydrogen, C₁-C₁₀-alkyl, C₃-C₁₀-cycloalkyl or C₆-C₁₅-aryl,

m is 1, 2, 3 or 4,

10 by reacting a transition metal complex of the formula (II)



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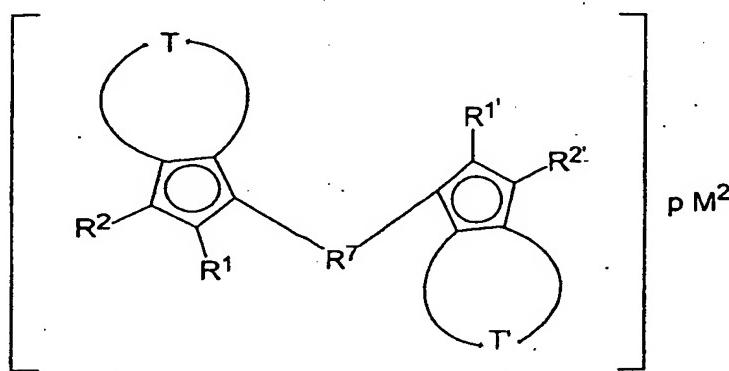
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where

X are identical or different and are each hydrogen, halogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, -OR¹⁷ or -NR¹⁷₂, where R¹⁷ are identical or different and are each C₁-C₁₀-alkyl, C₆-C₁₅-aryl, C₃-C₁₀-cycloalkyl, alkylaryl,
5 n is an integer from 1 to 4 and corresponds to the valence of M minus 2,

with cyclopentadienyl derivatives of the formula (III)

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where

M² is an alkali metal ion or alkaline earth metal ion,

and

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p is 1 when M² is an alkaline earth metal ion and is 2 when M² is an alkali metal ion,

and heating the resulting reaction mixture to a temperature in the range from -78 to +250°C.

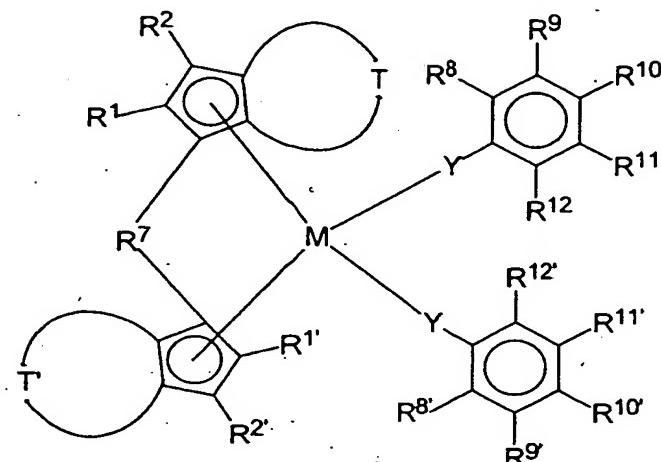
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2. A process as claimed in claim 1 for preparing racemic metallocene complexes of the formula (I)

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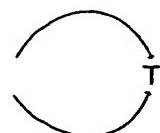
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(I)

where

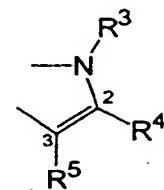
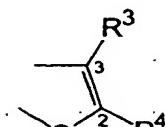
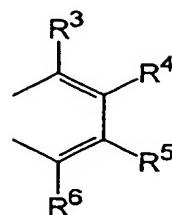
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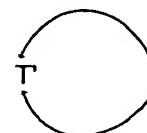
is a divalent group such as

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and

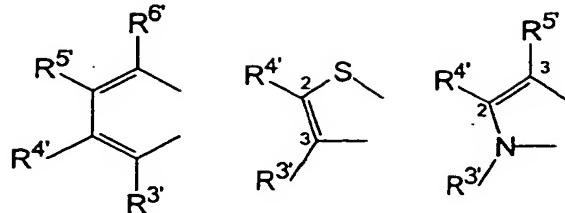
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is a divalent group such as

5



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and the substituents and indices have the following meanings:

M is titanium, zirconium or hafnium,

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R¹, R², R³, R⁴, R⁵, R⁶, R⁹, R¹⁰, R¹¹, R^{1'}, R², R³, R⁴, R⁵, R⁶, R⁹, R¹⁰, R¹¹

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are identical or different and are each hydrogen, halogen, C₁-C₂₀-alkyl, 3- to 8-membered cycloalkyl which may in turn bear a C₁-C₁₀-alkyl group as substituent, C₆-C₁₅-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, arylalkyl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part,

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-OR¹³, -SR¹³, -N(R¹³)₂, -P(R¹³)₂ or Si(R¹³)₃, where

R¹³ are identical or different and are each C₁-C₁₀-alkyl, C₆-C₁₅-aryl, C₃-C₁₀-cycloalkyl, alkylaryl, where the radicals mentioned may be partially or fully substituted by heteroatoms,

30

R⁸, R¹², R⁸, R¹² are identical or different and are each C₁-C₁₀-alkyl,

Y are oxygen -O-

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R⁷ is a $-[Z(R^{15})(R^{16})]_m-$ group, where

Z can be identical or different and are each silicon, germanium, tin or carbon,

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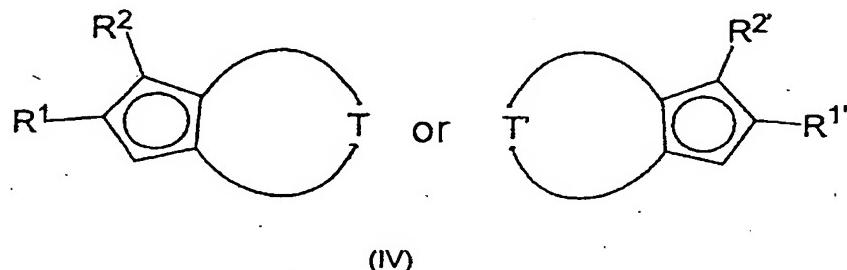
R¹⁵, R¹⁶ are each hydrogen, C₁-C₁₀-alkyl, C₃-C₁₀-cycloalkyl or C₆-C₁₅-aryl,

m is 1, 2, 3 or 4,

10 comprising the following steps:

a) deprotonation of a compound of the formula (IV)

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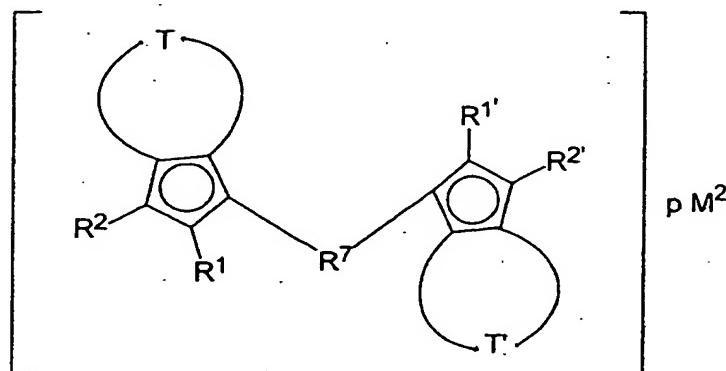
by means of a suitable deprotonating agent;

b) reaction of the deprotonated compound (IV) with a compound $R^7\text{Hal}_2$, where Hal is a halogen substituent such as F, Cl, Br or I, and subsequent repeat deprotonation by means of a suitable deprotonating agent to give the compound of the formula (III)

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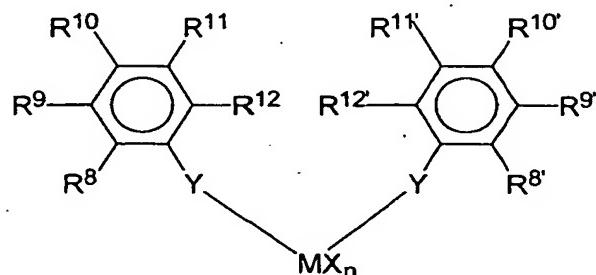
(III)

where
20 M^2 is an alkali metal ion or alkaline earth metal ion,
where

p is 1 when M^2 is an alkaline earth metal ion and is 2 when M^2 is an alkali metal ion, and R^7 is as defined above;

b) reaction of the compound of the formula (III) with a transition metal complex of
25 the formula (II)

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(II)

where
X are identical or different and are each hydrogen, halogen, C_1-C_{10} -alkyl, C_6-C_{15} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 40 6 to 20 carbon atoms in the aryl part, $-OR^{17}$ or $-NR^{17}R^{17}$, where R^{17} are identical

to 20 carbon atoms in the aryl part, $-OR^{17}$ or $-NR^{17}2$, where R^{17} are identical or different and are each C_1-C_{10} -alkyl, C_6-C_{15} -aryl, C_3-C_{10} -cycloalkyl, alkylaryl, is an integer from 1 to 4 and corresponds to the valence of M minus 2, and the other substituents are as defined above.

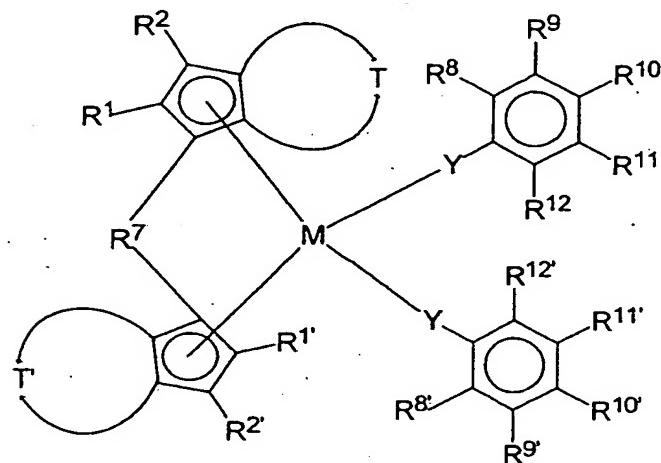
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3. A racemic metallocene complex of the formula (I)

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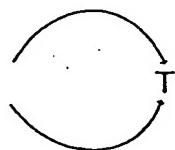
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(I)

where

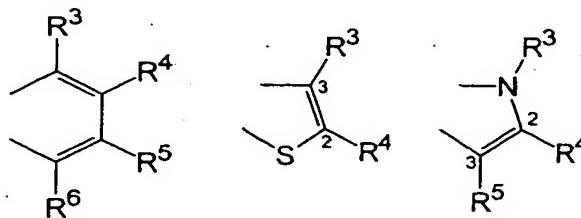
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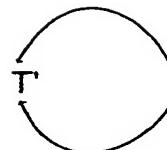
is a divalent group such as

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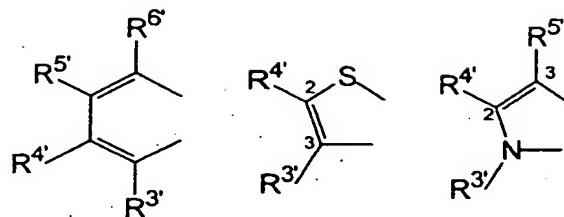
and



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is a divalent group such as

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and the substituents and indices have the following meanings:

M is titanium, zirconium or hafnium,

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$R^1, R^2, R^3, R^4, R^5, R^6, R^9, R^{10}, R^{11}, R^1', R^2', R^3', R^4', R^5', R^6', R^9', R^{10}', R^{11}'$ are identical or different and are each hydrogen, halogen, C_1-C_{20} -alkyl, 3- to 8-membered cycloalkyl which may in turn bear a C_1-C_{10} -alkyl group as substituent, C_6-C_{15} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, arylalkyl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, $-OR^{13}, -SR^{13}, -N(R^{13})_2, -P(R^{13})_2$ or $Si(R^{13})_3$, where

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R^{13} are identical or different and are each C_1-C_{10} -alkyl, C_6-C_{15} -aryl, C_3-C_{10} -cycloalkyl, alkylaryl, where the radicals mentioned may be partially or fully substituted by heteroatoms,

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$R^8, R^{12}, R^{8'}, R^{12'}$ are identical or different and are each C_1-C_{10} -alkyl,

35

Y are oxygen $-O-$

40

R⁷ is a $-\{Z(R^{15})(R^{16})\}_m-$ group, where

Z can be identical or different and are each silicon, germanium, tin or carbon,

5

R¹⁵, R¹⁶ are each hydrogen, C₁-C₁₀-alkyl, C₃-C₁₀-cycloalkyl or C₆-C₁₅-aryl,
and

m is 1, 2, 3 or 4.

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4. A process or complex as claimed in any of the preceding claims,
wherein the substituents R⁸, R^{8'} and R¹², R^{12'} are identical and are selected from among
methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl and tert-butyl, particularly preferably
methyl.

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5. A process or complex as claimed in any of the preceding claims,
wherein the substituents R¹ and R^{1'} are identical or different and are each hydrogen or
methyl.

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6. A process or complex as claimed in any of the preceding claims,
wherein M is zirconium.

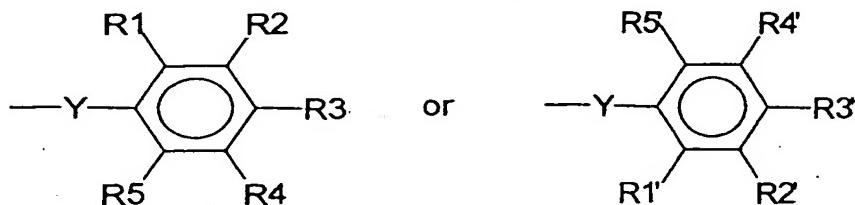
5 7. A process or complex as claimed in any of the preceding claims,
wherein M² is magnesium or lithium.

8. A process or complex as claimed in any of the preceding claims,
wherein R⁷ is a dimethylsilyl group or an ethanediyl group.

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9. A process as claimed in any of claims 1, 2 and 4 to 8,
wherein, in a further step, the compound of the formula (I) is reacted with suitable re-placement reagents to replace at least one of the groups

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by halogen substituents such as F, Cl, Br or I or by linear, branched or cyclic C₁₋₁₀-alkyl substituents.

25 10. A process as claimed in claim 9,

wherein the replacement reagents are selected from among aliphatic and aromatic carboxylic acid halides such as acetyl chloride, phenylacetyl chloride, 2-thiophenacetyl chloride, trichloroacetyl chloride, trimethylacetyl chloride, O-acetylmandelyl chloride, 1,3,5-benzene tricarboxylic chloride, 2,6-pyridinecarboxylic chloride, tert-butylacetyl chloride, chloroacetyl chloride, 4-chlorobenzacetyl chloride, dichloroacetyl chloride, 3-methoxyphenylacetyl chloride, acetyl bromide, bromoacetyl bromide, acetyl fluoride, benzoyl fluoride, SOCl₂, silicon tetrachloride, organoaluminum compounds such as tri-C_{1-C₁₀}-alkylaluminums, in particular trimethylaluminum, triethylaluminum, tri-n-butylaluminum, tri-isobutylaluminum, and dialkylaluminum chlorides, aluminum sesquichlorides, methylaluminum dichloride, dimethylaluminum chloride, aluminum trichloride and ethylaluminum dichloride and combinations thereof.

11. A process as claimed in claim 9,
wherein replacement reagents used are HF, HBr, HI, preferably HCl, as such or as solutions in water or organic solvents such as diethyl ether, DME or THF.

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12. A process as claimed in any of claims 1, 2 and 4 to 11,
wherein the deprotonating agent is selected from among n-butyllithium, tert-butyllithium, sodium hydride, potassium tert-butoxide, Grignard reagents of magnesium, magnesium compounds such as, in particular, di-n-butylmagnesium, (n,s)-dibutylmagnesium and other
10 suitable alkaline earth metal alkyl and alkali metal alkyl compounds.

10

13. A process as claimed in any of claims 1, 2 and 4 to 12,
wherein no intermediates are isolated during the process.

15 14. A complex as claimed in claim 3 selected from among dimethylsilylbis(1-indenyl)zirconium bis(2,4,6-trimethylphenoxy), dimethylsilylbis(2-methyl-1-indenyl)zirconium bis(2,4,6-trimethylphenoxy), dimethylsilylbis(2-methyl-1-indenyl)zirconium bis(2,6-dimethylphenoxide), dimethylsilylbis(2-methyl-1-indenyl)zirconium bis(2,6-dimethyl-4-bromophenoxy) and ethanediylbis(1-indenyl)zirconium bis(2,4,6-trimethylphenoxy).

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15. The use of a racemic metallocene complex as claimed in any of claims 3 to 8 and 14 as a catalyst or as a constituent of a catalyst for the polymerization of olefinically unsaturated compounds or as a reagent or catalyst in stereoselective synthesis.

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